PHYSICAL REVIEW B **67**, 100406(R) (2003)

Mean-field behavior with Gaussian fluctuations at the ferromagnetic phase transition of $SrRuO_3$

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(Received 9 December 2002; published 28 March 2003)

Specific heat, resistivity, and magnetization have been measured through the ferromagnetic critical point for single-crystal $SrRuO_3$. All data are well fitted to small reduced temperatures with mean-field critical exponents including Gaussian fluctuations. The specific heat and temperature derivative of resistivity scale with each other, confirming the Fisher-Langer relation. A long magnetic correlation length due to $4d$-electron itinerancy is likely responsible for the mean-field behavior.

DOI: 10.1103/PhysRevB.67.100406 PACS number(s): 75.40.−s, 64.70.−p, 75.30.−m, 75.50.−y

Metallic oxides, including the ruthenates, show a wide variety of remarkable cooperative behavior attributed to narrow bands and correlated electron behavior. $SrRuO_3$ is a good example of this, with an extraordinarily high ferromagnetic ordering temperature T_c for a $4d$ metal, transport properties whose magnitude and strong temperature dependence suggest a breakdown of Fermi liquid theory (so-called ''bad metal'' behavior), enhanced low-temperature specific heat, and an anomalous vanishing of magnetism on substitution of isovalent Ca for Sr.[1–5] Despite the more extended nature of the $4d$ electrons, $SrRuO_3$ displays features similar to the high-T_c oxides and reflects anomalous behavior often associated with non-Fermi-liquid behavior. In contrast to many of the non-Fermi-liquid systems, however, $SrRuO_3$ is not near a quantum critical point. The anomalous transport behavior reported for $SrRuO_3$ may be related to strong local hybridization that drives the response at high temperatures but becomes less relevant at low temperatures where Fermi-liquid behavior is expected to be recovered.[6]

Magnetic properties show similar possibly related anomalies. Treated in a local moment picture, with crystal field splittings, the Ru^{4+} ions are expected to be in a low spin state $S=1$, but there is considerable evidence that an itinerant band magnetism picture is a more appropriate description. High-temperature susceptibility measurements ($T > T_c$) give an effective moment $p=2.6\mu_B$ per Ru ion, which agrees well with the local moment $S=1$ per Ru^{4+} ion ($2[S(S+1)]^{0.5}=2.83\mu_B$).[5,7,8] However, the low-temperature low-field magnetization p_s is $1.1\mu_B$, significantly lower than the $2\mu_B$ expected from $S=1$, and reaches only $1.6\mu_B$ even at 30 T.[2,5,8] Neutron scattering confirms this low moment [$m=1.19\pm0.13$ (statistical) ±0.15 (systematic)], and suggests that of order $\frac{3}{4}$ of the moment is associated with the Ru site and $\frac{1}{4}$ with the oxygen sites.[9] Band theory predicts $1.45–1.7\mu_B$ due to splitting of t_{2g} levels.[3,10,11] The ratio of $p/p_s=2.4$ suggests an electronic state intermediate between the itinerant and localized limits.[12]

Analysis of the paramagnetic/ferromagnetic phase transition might be expected to shed light on this issue of moment localization at T_c, but has been controversial. Critical analysis of magnetization exponents β and γ by Klein and coworkers were interpreted as Ising-like, consistent with the anisotropy of thin-film $SrRuO_3$. Using Fisher-Langer theory to analyze their resistivity measurements, however, they found anomalous specific heat critical exponents $\alpha \neq \alpha'$, and suggested that this implies a breakdown of Fisher-Langer theory, evidence of the exotic nature of this material.[13,14] Their data were reanalyzed by Roussev and Millis as consistent with conventional theory, but the original authors rejected this reinterpretation.[15,16] There has been no report on the critical behavior of bulk samples, where T_c is 10–15 K higher, and the only direct specific heat measurements are on samples where inhomogeneity significantly broadened the transition.[3,17] In this paper, we report high-precision magnetization, resistivity, and specific heat measurements of single-crystal bulk $SrRuO_3$ through T_c.

Single-crystal samples of $SrRuO_3$ with a resistivity ratio $R(300\,\mathrm{K})/R(2.2\,\mathrm{K}) \approx 100–140$ were prepared by a flux growth technique at 1500 °C. After slow cooling to 1350 °C, the samples were rapidly quenched through the cubic to tetragonal transition to orthorhombic transitions [between 800 and 975 °C (Ref. 18)] to room temperature, a technique used in $YBa_2Cu_3O_{6+\delta}$ to avoid twinning. Single-crystal x-ray analysis of five $SrRuO_3$ crystals from the same batch used in these experiments showed them to be untwinned. Further details of sample preparation and characterization are described in Ref. 5. In the present work, the magnetization M of a single crystal sample ($0.5\times0.5\times0.5\,\mathrm{mm}^3$, 883 μg) as a function of applied field H_a and temperature T was measured in a superconducting quantum interference device (SQUID) magnetometer. M was measured with H applied along the easy axis, found by rotating the sample around all three directions to find the maximum magnetization at 1 T at 160 K, just below T_c. The anisotropy at 160 K is small compared to that at 5 K,[5] as expected; at 1 T, the easy axis $M=7.9\times10^{-3}$ emu, intermediate axis $M=7.8\times10^{-3}$ emu, and hard axis $M=7.0\times10^{-3}$ emu. The hard axis was along the sample c axis, as previously seen. The demagnetization factor $D=0.49$ was determined from the slope of the low-field M vs H_a data, yielding the internal field $H=H_a-4\pi DM$; but the value of D has little effect on the analysis discussed below. The resistivity was measured with a standard four-probe ac bridge technique and the specific heat was measured with a low mass calorimeter using the relaxation

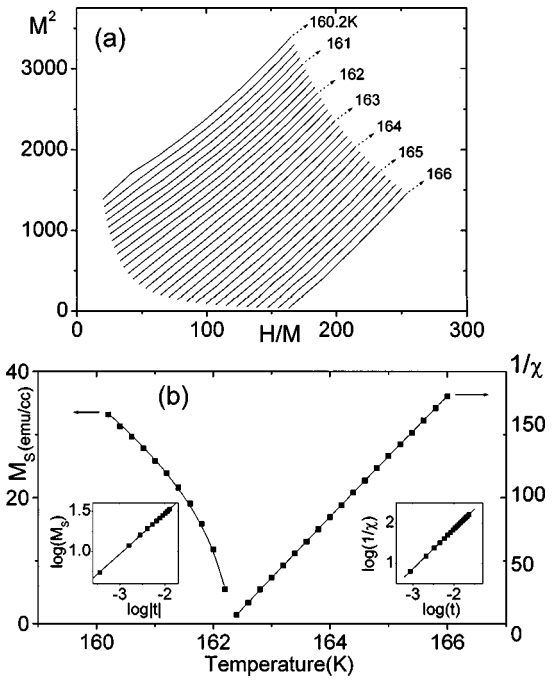

FIG. 1. (a) M^2 vs H/M for single crystal $SrRuO_3$ from $T=160$ to 166 K in 0.2-K steps. (b) M_S and $1/\chi$ [from intercepts in (a)] vs T. Insets: log-log plots for M_S and $1/\chi$ vs reduced temperature t.

method. Near a second-order ferromagnetic phase transition, the specific heat C_p, spontaneous magnetization [$M_s \equiv M(H=0)$], and initial magnetic susceptibility ($\chi \equiv \partial M/\partial H|_{H=0}$) show power-law dependence on the reduced temperature, $t \equiv (T-T_c)/T_c$ with critical exponents α, β, and γ, respectively, and at T_c $M(H) \propto H^{1/\delta}$.

$M(H)$ is shown in Fig. 1 as an M^2 vs H/M Arrott plot for T near T_c. The isothermal curves are very linear, suggesting mean-field behavior with $\beta=0.5$ and $\gamma=1$. To further refine these values, as discussed extensively in Refs. 8 and 19, we use an iterative modified Arrott plot scheme to obtain $T_c = 162.26$ K, $\beta = 0.50 \pm 0.03$ (from $\log M_s$ vs $\log t$) and $\gamma = 0.99 \pm 0.03$ (from $\log 1/\chi$ vs $\log|t|$), as shown in the insets of Fig. 1. To obtain δ, we plot M vs H for the two closest measured isotherms 162.2 and 162.4 K in Fig. 2; the inverse slope of $\log M$ vs $\log H$ (shown in the inset) gives $\delta = 3.21$ and 2.85, respectively. $\delta = 3.10 \pm 0.3$ was approximated by

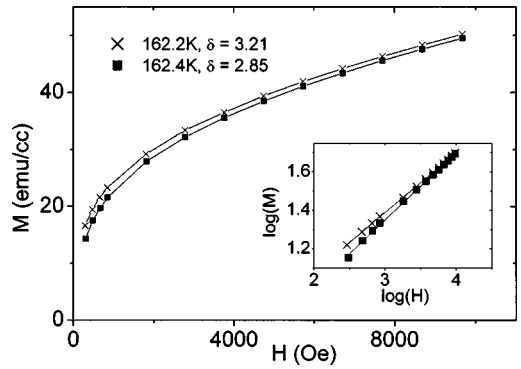

FIG. 2. M vs H at 162.2 and 162.4 K, closest to $T_c = 162.26$ K. Inset: $\log(M)$ vs $\log(H)$.

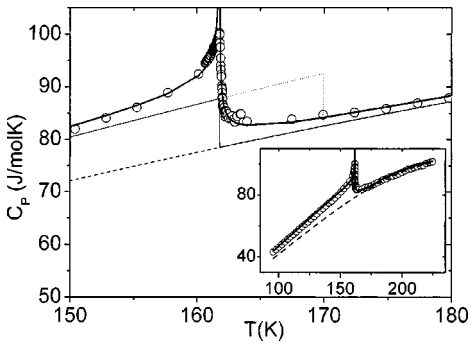

FIG. 3. C_p data (open circles), polynomial background $C_{\rm poly}$ (dashed line). Dotted line: calculated $C_{\rm MF}$ that conserves entropy, truncated above T_c to give a mean-field contribution to fit (thin line). Thick line: fit to C_p including Gaussian fluctuations. Inset: C_p data, fit, and $C_{\rm poly}$ in wider temperature range.

interpolation; this value is within error bars of the mean field value of 3.

The specific heat C_p of a ($0.1\times0.6\times0.6$ mm^3, 210 μg) bulk single-crystal sample of $SrRuO_3$ is shown in Fig. 3. The data were taken by a relaxation method, using sensitive SiN membrane-based microcalorimeters, as described in Ref. 19, and agree well with data shown in Refs. 3 and 17. The transition is, however, significantly sharper and clearly shows signs of fluctuations (upward curvature). The data were fitted in two ways: critical fluctuation analysis using a smooth background with a grid search method to minimize χ^2, and a mean-field model with Gaussian fluctuations. The former method (described in Ref. 19) gave a good fit to the data, as shown in Fig. 4, with $\alpha=\alpha'=0.084\pm0.04$ and amplitude ratio $A/A'=0.63\pm0.2$, within error bars of Ising values $\alpha=\alpha'=0.1$ and $A/A'=0.524$, to low reduced temperatures (0.0002 above T_c and 0.001 below T_c).[16] Ising critical behavior is, however, inconsistent with the mean-field values found for the three magnetization exponents. We suggest instead that critical fluctuations should not be observed until extremely small reduced temperatures ($<10^{-4}$) are reached because of the itinerant nature of the magnetism and consequently long correlation length. We therefore fit the data to mean-field behavior, including the effect of three-

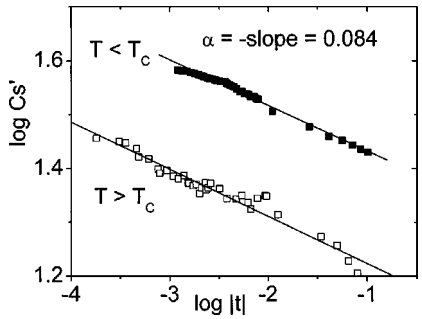

FIG. 4. $\log C_s'$ vs $\log|t|$, where $C_s' = C_p$ minus the linear background $A+Bt$ with $A=61.555$ and $B=103.12$, found from a χ^2 grid search minimization procedure (described in Refs. 8, 16, and 19). Negative slope $\alpha=\alpha'=0.084\pm0.04$ (error bars from the 2σ contours of χ^2). Although fit is good, the fit shown in Fig. 3 (mean-field plus Gaussian fluctuations fit) is more consistent with critical exponents β, γ, δ.

dimensional (3D) Gaussian fluctuations.[20] Gaussian fluctuations are associated with the variance in M ($\langle \Delta M^2 \rangle = \langle M^2 \rangle - \langle M \rangle^2$); these occur on a short length scale and do not change the mean value $\langle M \rangle$. They have therefore no significant effect on magnetization, but give a contribution to C_p with the same form as that for critical fluctuations but with a universal exponent $\alpha = \alpha' = 0.5$.

Following the procedure outlined by Inderhees *et al.* for analysis of $YBa_2Cu_3O_{7-\delta}$,[21] we fit $C_p^{\pm}(t) = (A_{\pm}/\alpha)|t|^{-\alpha} + C_{\mathrm{MF}} + C_{\mathrm{poly}}$ with $\alpha = 0.5$, + corresponds to $t > 0$, − corresponds to $t < 0$, and C_{poly} is a polynomial fit to the background (taken from data far from the transition). The mean-field contribution $C_{\mathrm{MF}} = -\frac{3}{4} N k_B T_c \partial(m^2)/\partial T$, where N is the number of magnetic electrons per mole of $SrRuO_3$ (a parameter fit by the C_p data) and $m(T) = M(T)/M(0)$ is obtained by numerically solving the mean-field magnetization equation for spin $S = 1$.[22] This yields C_{MF} in units of T/T_{MF}, where $T_{\mathrm{MF}} \sim T_c$. $T_c < T_{\mathrm{MF}}$ because fluctuations suppress T_c from its calculated mean-field value. Again following Ref. 21, $T_{\mathrm{MF}} = 169.92$ K, higher than the real $T_c = 161.79$ K, is chosen such that the magnetic entropy $NR\ln(3)$ is conserved (i.e., fluctuations suppress the transition, but conserve entropy). C_{MF} below the real T_c is then fitted with a fifth-order polynomial. Figure 3 shows the resulting C_{MF} and C_{poly}.[23] After subtracting C_{MF} and C_{poly}, C_p is fitted to Gaussian fluctuations with critical exponent $\alpha = 0.5$, giving $N = 0.6$ mol and $A/A' = 0.68$. Data points very close to T_c were removed from the fit due to presumed rounding. $N = 0.6$ per mole is less than 1, the expected number of $S = 1$ Ru ions per molecular unit if all electrons of Ru ions are localized, but is consistent with the reduced low-temperature low-field magnetization $p_s = 1.1\mu_B$, i.e., 0.6 per mole of $S = 1$ Ru ions $= 0.6 \times 2\mu_B = 1.2\mu_B$. The amplitude ratio $A/A' = n/2^{d/2}$ in a Gaussian fluctuation model where n is the number of spin components and d is the dimensionality.[20] Our value of $A/A' = 0.68$ is close to 0.71, the $n = 2$ value (fluctuations of XY-type spins), consistent with the anisotropy of bulk $SrRuO_3$ which is 5–10 T with easy axes in the (001) plane.[5,24]

In order to understand the significant differences between our analysis of C_p and that reported by Klein *et al.*,[13] we also made high-precision resistivity measurements $\rho(T)$ on a bulk sample taken from the same processing batch. Fisher and Langer[25] showed that short-range spin fluctuations near T_c increase the carrier scattering rate and cause $d\rho/dT$ to scale with the same critical exponent α as the specific heat: $d\rho/dT \sim |t|^{-\alpha}$. Figure 5 shows the comparison among the directly measured C_p with the polynomial background shown in Fig. 3 subtracted [i.e., $C_s(T) = C_p(T) - C_{\mathrm{poly}}$], $d\rho/dT$ on the bulk sample, and $d\rho/dT$ for the thin film sample digitized from the data shown in Ref. 13. The raw C_p and ρ data for the bulk samples showed a 0.26-K difference in T_c, likely associated with the different thermometers used in the two separate experimental apparatuses of these measurements (commercial thermometers do not have absolute calibrations better than 1%; this 1% absolute difference, however, should have no impact on the analysis, which requires accurate relative temperatures only). A temperature

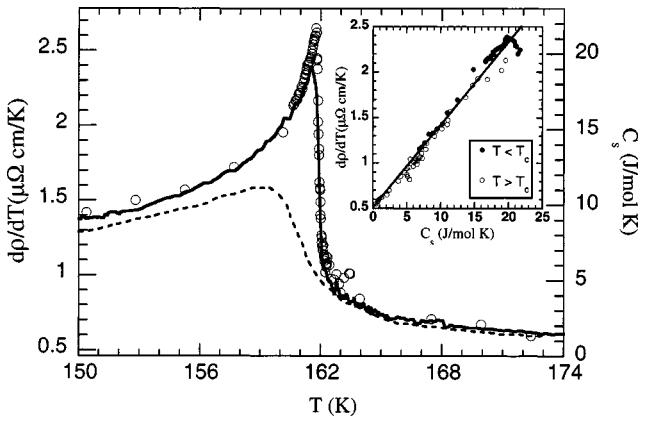

FIG. 5. Solid line and left axis: $d\rho/dT$ of bulk single crystal sample; T shifted by −0.26 K, as discussed in text. Open circles and right axis: $C_s = C_p - C_{\mathrm{poly}}$ from Fig. 3. Dotted line: $d\rho/dT$ of thin film digitized from Ref. 13; T shifted by 9.1 K due to different T_c. Inset: $d\rho/dT$ vs C_s.

shift for $d\rho/dT$ of −0.26 K was made in Fig. 5 to account for this difference. The overlap between C_S and $d\rho/dT$, as shown in Fig. 5 for the bulk samples, is a strong confirmation of the Fisher-Langer relation and the existence of fluctuations near T_c; to the best of our knowledge, this confirmation has not been previously seen in magnetic materials for which Gaussian fluctuations dominate (as opposed to materials such as Fe, Ni, or Cr where critical fluctuations dominate). The inset of Fig. 5 shows $d\rho/dT$ vs C_s and demonstrates a remarkable proportionality. Figure 5 also shows the thin-film $d\rho/dT$ data from Ref. 13; data were shifted by +9.1 K, to account for the lower T_c (150 K) of the films. This data show a peak at T_c, which is significantly broader than the bulk sample data, but matches well away from T_c. From these data, it appears that the analysis made in Ref. 13 is outside the critical regime, and may be negatively impacted by sample inhomogeneity or strains in the thin films grown on $SrRuO_3$.

The data shown in Figs. 1–5 thus present an extremely consistent picture of a transition dominated by mean-field behavior down to remarkably small reduced temperatures for a magnetic phase transition. Saturation magnetization M_s and inverse susceptibility $1/\chi$ are well fitted with mean-field parameters $\beta = 0.5$ and $\gamma = 1$ over a wide temperature range. This result is quite different than that of the thin film found in Ref. 14, in which an Ising fluctuation model was suggested, but the present data are taken to significantly smaller reduced temperatures ($t = 0.002$ vs 0.01), and on samples of higher homogeneity (judging from the breadth of T_c shown by the specific heat peak of Fig. 4 and the extremely large resistivity ratio of the single-crystal samples used in this study). The $M(H)$ exponent $\delta = 3$ is also consistent with mean-field behavior. The specific heat is shown to scale with $d\rho/dT$, indicative of fluctuation effects; these can be fitted within a mean-field model including the effects of Gaussian fluctuations. As discussed in Ref. 26, critical exponents associated with the average value of $\langle M \rangle$, i.e., β, γ, and δ, are not affected by Gaussian fluctuations, but C_p and $d\rho/dT$ are affected not only by $\langle M \rangle$ but also by $\langle \Delta M^2 \rangle$.

Specific heat was here fitted with a mean-field local moment $S=1$ model, plus Gaussian fluctuations. As discussed in the introduction, the magnetic properties of $SrRuO_3$ show behavior between that of a local moment and itinerant model. It could, therefore, be of interest to determine C_p in a mean-field itinerant electron model, including effects of band structure. This was not attempted in the present work, and is not likely to significantly affect the critical analysis near T_c except to change the mean-field parameters N, ΔC, and T_{MF}. This statement is based on fits to $C_p(T)$ with an $S=\frac{1}{2}$ local moment mean-field model; because of the linearity of C_p near T_c in mean-field models, only the overall scaling factor N significantly changed.

Gaussian fluctuation analysis is valid in the same temperature range as mean-field theory and hence has the same Ginzburg criterion for validity: $t_G > (\frac{1}{32}\pi^2)(k_B/\Delta C \xi_0^3)^2$, where ΔC is the specific heat discontinuity and ξ_0 is the zero-temperature correlation length. True critical fluctuations are only significant for $t < t_G$. Taking $\Delta C = 9.4$ J/mol K from C_{MF} and using the smallest $t=0.0003$ in our experiment yield a lower boundary for ξ_0 of 7 Å.

In conclusion, we have performed magnetization, resistivity, and specific heat measurements on single-crystal $SrRuO_3$ to study the critical behavior of the ferromagnetic phase transition at $T_c \sim 160$ K. An Arrott plot method was used to obtain magnetization critical exponents $\beta = 0.50 \pm 0.03$, $\gamma = 0.99 \pm 0.03$, and $\delta = 3.1 \pm 0.3$, all within error bars of mean-field values down to reduced temperatures of 0.0003. The specific heat and the temperature derivative of the resistivity were shown to scale with each other and were well fitted using *either* critical fluctuation *or* mean-field including Gaussian fluctuations methods, but only the latter is consistent with the other mean-field critical exponents. The observation of mean-field behavior to 0.0003 yields a lower boundary of the correlation length $\xi_0 > 7$ Å. We argue that the itinerancy of the Ru electrons causes the long correlation length, which in turn causes mean-field behavior to persist to strikingly small reduced temperatures compared with the conventional $3d$ ferromagnetic metals, further evidence of the unique nature of this $4d$ ferromagnet.

D.K., B.L.Z., and F.H. thank the NSF for support (DMR 97-05300 and 02-00000); S.M., G.C., and J.E.C. acknowledge partial support from the National High Magnetic Field Laboratory through NSF Cooperative Agreement DMR-0084173 and support provided by the state of Florida.

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[16] In conventional critical analysis, α is obtained from the best fit of $C_p^{\pm} = (A_{\pm}/\alpha)|t|^{-\alpha} + B + Ct$ for small t ($t < t_G$). $A_{\pm}$ are amplitude coefficients. $B+Ct$ includes both a physical smooth background of phonons, etc., and a constant offset which is part of fluctuation theory. If $\alpha > 0$, $C_p^{\pm} > B + Ct$ and diverges at T_c, but if $\alpha < 0$, $(A_{\pm}/\alpha)|t|^{-\alpha}$ vanishes at T_c and $C_p^{\pm} < B + Ct$ with a cusp. If B is required to be $< C_p^{\pm}$, as in Ref. 12, negative values of α, e.g., the 3D Heisenberg exponent -0.1, are not possible. The reanalysis in Ref. 15 properly includes B, but constrains α, which was the basis of its rejection by the original authors. In the present paper, the fit in Fig. 4 used a grid search method to find the best values for B and C, assuming that $B_+ = B_-$, i.e., no discontinuity at T_C. We also fit the data allowing a discontinuity (B_+ B_-); this resulted in $\alpha < 0$, which is not allowed with a discontinuity so this fit was discarded as unphysical. For the mean-field plus Gaussian fluctuations fit shown in Fig. 3, the background is constrained by mean-field theory and has a discontinuity in both slope and offset.

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[23] In the mean-field fitting approach, $C_P^{\pm}(t) = C_{\mathrm{MF}} - C_{\mathrm{poly}} + (A_{\pm}/\alpha)|t|^{-\alpha}$, with $\alpha = 0.5$. To get $C_{\mathrm{MF}}(T)$, we solved the transcendental equation for $M(T)$ for $S=1$ [Eq. (2.3.11) in Ref. 22], and used Eq. (2.3.8) to get C from $M(T)$. $C_{\mathrm{MF}}(T)$ was approximated by a fifth order polynomial: $C_{\mathrm{MF}}(T) = Nk_B [-0.211\,26 - 0.110\,64(T/T_{\mathrm{MF}}) + 6.84174(T/T_{\mathrm{MF}})^2 - 9.00769 (T/T_{\mathrm{MF}})^3 + 6.215\,81(T/T_{\mathrm{MF}})^4 - 1.728\,95(T/T_{\mathrm{MF}})^5]$. After subtracting C_{MF} from C_P with a choice of (N, T_{MF}), data far from T_C were fit to a third order polynomial background $C_{\mathrm{poly}}(T)$, and the difference fit to $(A_{\pm}/\alpha)|t|^{-\alpha}$; this process was iterated until a convergent solution was found ($T_{\mathrm{MF}} = 169.92$ K as described in the text; $N = 0.6$ was chosen such that $C_P^{\pm}(t)$ can be fitted with $\alpha = 0.5$ [if $N < (>) 0.6$, then $\alpha < (>) 0.5$]; $C_{\mathrm{poly}} = 27.587\,89 - 0.514\,34T + 0.008\,268T^2 - 0.000\,020\,122\,3T^3$).

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